

Study on Biochemical Methane Potential and Engineering Application of Sludge Dehydrated Water through Hydrothermal Drying Treatment

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Abstract

The Hohhot sewage sludge dehydrated water (SDW) through hydrothermal drying treatment was studied in this paper, which was evaluated by Biochemical Methane Potential (BMP) test as well as the guidance for a biochemical methane potential project. The results showed that under 35 degree, after continuous 21 days fermentation, the sludge dehydrated water performed the maximum cumulative gas production (9450 mL) with the concentration of 20 g COD/L. With the increase of concentration of sludge dehydrated water, both unit biogas production and methane conversion rate rose at first and then fell, and it achieved 499.8 mL/G COD which was the maximum of 10 g COD/L slurry. According to the optimal results of commercial project in Hohhot, the efficiency of 20 g COD/L sample, 83.42 tons of sludge dehydrated water if all the loading of COD was degraded were calculated to produce 342 m³ methane, corresponding to the heat from 239.5 kg standard coal, which could be used for recycling.

Key words

Hydrothermal Drying; Sludge Dehydrated Water; Biochemical Methane Potential; Methane

Introduction

As a new applied technology in the sludge treatment area, hydrothermal drying technology for sludge has attracted much attention both at home and abroad in recent years, with advantages such as decrement of sludge volume, enhancement of anaerobic digestion potential, non-toxic, green, and recycling, etc. However, there are a large mass of raw sludge produced without stable processing each year, and it was seriously disrupted in between sludge treatment and wastewater

treatment. Sludge contains cytoplasm, colloid, and macromolecular organism, etc. so it has to be the key to the cell disruption technology to improve sludge de-watering performance.

Hydrothermal drying technology holds the capabilities, for instance, it can break up microbiological flocks, rupture cells, and dissolve solid organics or resolvable macromolecular organism to molecule organism, change the characteristics of sludge moisture fundamentally, improve the anaerobic digestion performance of sludge, and enhance the efficiency of anaerobic digestion as well as methane production. As the residual product, sludge dehydrated water is also getting much attention for its high concentration of organics and nutrition, which has a high resources potential. Small-scale and large-scale sludge experiment have been performed by means of hydrothermal drying technology, and the result showed that the optimum reaction temperature was 190°C and the optimum reaction time was 30 minutes. With these optimum operating conditions, the moisture content of the solid residue was reduced to less than 40% by the hydrothermal treatment followed by the mechanical dehydration, and the moisture content of the solid residue could be reduced to 20% and 10% by 24 hours and 48 hours of natural drying, respectively. Meanwhile it would be a huge resource recycling potential through component analysis of sludge dehydrated water.

The sewage sludge dehydrated water was studied as the object of this experiment, which was researched on its feasibility of methane production, and to get the

better reaction conditions. At the same time, it was essential to investigate technical feasibility and economic and rational research for this technical route, in order to improve the hydrothermal drying technical chain of sludge, to achieve closed-cycle treatment of both wastewater and sludge through hydrothermal drying method, and to achieve the maximum of the recycle of resource, in combination with some engineering projects of biochemical methane potential from sludge dehydrated water.

Experiment

Materials

1) Sludge Dehydrated Water

In this study, the sludge dehydrated water (SDW) was derived from the sludge off-Hohhot sewage treatment plant (20% of total solid), which was the residual fluid after hydrothermal drying treatment (Table 1). It could be seen that this SDW had a better biodegradability to be used as the substrate (or zymotic fluid) of methane production, which had the ratio of $BOD_5/COD_{cr} \approx 0.38$.

TABLE1 CHARACTERISTICS OF THE SDW

pH	SS /mg·L ⁻¹	TP /mg·L ⁻¹	NH ₃ -N /mg·L ⁻¹	COD _{cr} /mg·L ⁻¹	BOD ₅ /mg·L ⁻¹
6.75	1.384	0.101	1.8	41.82	15.73

2) Inoculated sludge (IS)

Inoculated sludge was collected from the anaerobic digester of Beijing sewage treatment plant, which was added to glucose with 5000mg/L dosage for one week domestication.

Facilities

In this experiment, the anaerobic methane-producing system with simple glass bottles was adopted to simulate anaerobic fermentation process, in order to provide data support for future engineering application. The apparatus was installed as Fig.1 shown below, and then its leak proofness was inspected.

2.5L CSTR (continuous stirred tank reactor) tanks were used as anaerobic reactors. Certain volume of SDW was added into each bottle, diluted with distilled water to 1.5L, then inoculated with flocculent anaerobic sludge respectively according to the inoculation quantity of $COD_{SDW}:VSS_{IS}=4:1$, and in the end filled nitrogen gas for 3 minutes to eliminate oxygen inside. The biogas produced by anaerobic fermentation was measured by gas flowmeter.



FIG.1 EXPERIMENTAL DEVICE OF BIOCHEMICAL METHANE POTENTIAL

Methods

1) Biochemical Methane Potential test

Table 1 showed that the concentration of COD and ammonia nitrogen is relatively high for methanogens' normal growth, and it was essential for the SDW with gradient dilution. Anaerobic bottles were numbered consecutively from No.1 to No.6, among which No.1~No.4 were the zymotic fluids with 1, 2, 4, 8 times dilution of the raw SDW, similarly, No.5~No.6 were the comparison sample (CP., containing 375mL raw fluid and 1125mL distilled water) and the blank one (BK., containing 1500mL distilled water and 125mL inoculated sludge).

TABLE2 CHARACTERISTICS OF THE SDW

No.	COD/g·L ⁻¹
1	41.82
2	20.91
3	10.45
4	5.23

The alkalescency of the zymotic fluid was adjusted to pH of 7.5~8.0 by means of 3mol/L NaOH solution, and reactors installed as shown in Fig.1, were placed in constant temperature incubator with 35degrees Celsius [15]. Little water was added into 6 graduated cylinders in order to make the liquid level coincide with zero graduation, and two records of methane yield at 8:00 and 16:00 every day were kept with slowly vibrating anaerobic bottles for about 30min one time, in order to avoid the emergency of partial acidification. After the completion of methane production, pH values were tested for all of zymotic fluids.

2) Sludge Hydrothermal Drying pretreatment

This project could reduce the water content (WC) of

sludge from 80% to 20% through hydrothermal drying method. At first, wet sludge was added into steam reaction kettle, where heat was exchanged with saturated steam at 190°C for 30min. Then, the sludge after hydrothermal drying with 85% water content, had such liquidity as to gravitationally flow into pressofiner for mechanical dehydration, in addition, the SDW was the test sample.

Analysis method and Instrument

Cumulative biogas yield and daily biogas yield of SDW were calculated by the volume of alkaline effluent. COD_{cr} was tested by the potassium dichromate method, using HACH DR/890 water quality analyzer. Ammonia nitrogen was measured by the sodium's reagent spectrophotometry method, using HACH IL500 auto-analyzer. The value of pH was tested by Laser PHS-3C, and suspended solid (SS) and BOD₅ were tested by means of standard methods.

Results and Discussion

Biochemical Methane Potential of Sludge Dehydrated Water

1) Cumulative Biogas Yield and Daily Biogas Yield

The main propose was to investigate biochemical methane potential of the SDW, by keeping records of alkali liquor volume regularly, calculating cumulative and daily biogas yield.

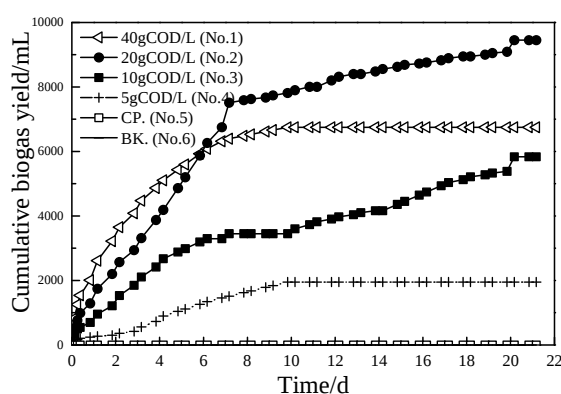


FIG.2 CUMULATIVE METHANE PRODUCTION WITH DIFFERENT COD OF SLUDGE DEHYDRATED WATER

Cumulative biogas yield with different COD loadings of SDW was shown in Fig.2. At the beginning of 6 days, all except compared and blank samples had higher biogas yield, the order of which was No.2>No.1>No.3>No.4. The rate of biogas production began to slow down for the first time after 6 days fermentation. However, the yield of No.2 sam-

ple rapidly increased again after 10 days, reaching the maximum of 790mL, 39.8% larger than the second one (No.3). The ultimate order of cumulative biogas yield was No.2>No.3>No.1>No.4.

In the initiating stage of fermentation, No.1 sample had the top speed of biogas production but with normal cumulative biogas production. The reason might be with too high concentration of ammonia nitrogen (1800mg/L) and the nearly neutral zymotic fluid in the end, inhibition effect occurred after 6 days fermentation to methanogens rather than acidification generated by acetic acid bacteria, which led to the low biogas production efficiency (6750mL cumulative biogas yield). No.2 sample had a rapid speed at the beginning, but stagnated during 6th~10th days, and then came up to significant biogas efficiency again. It might be because the mixed anaerobic fermentation bacteria could better adapt to this zymotic fluid with the organic loading conditions, which could breed in abundance and cooperate with methanogens to convert organism from the zymotic fluid. The methane-producing curve of No.3 sample was similar to No.1, both of which appeared dead time from 6th to 10th, then produced biogas again, and ultimately reached 5825mL in the 17th day.

Therefore, No.2 sample having the top speed of biogas production in the initiating stage as well as the largest biogas yield, achieved biogas summit again after merely 3 days, and was significantly better than No.3 and No.1 samples account of biogas production efficiency and cumulative biogas production, which presented important references for reasonable adjustment to the organic loading of zymotic fluid in engineering application.

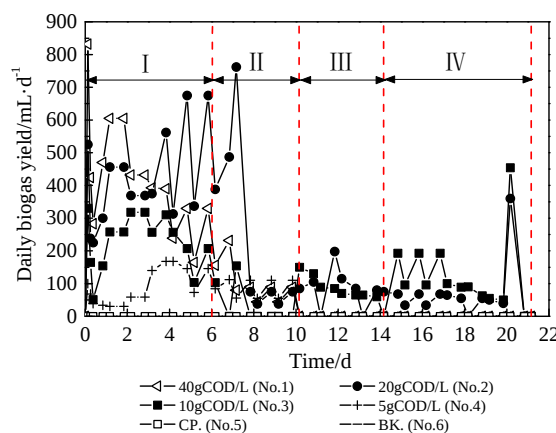


FIG.3 DAILY METHANE PRODUCTION WITH DIFFERENT COD OF SLUDGE DEHYDRATED WATER (SDW)

As it was seen in Fig.3 that the daily biogas production of No.1 sample had the maximum production during initial 6 days (gas peak period: I), and then quickly dropped to an end in the 11th day. No.2 and No.3 samples quickly achieved each biogas summit initially, gradually stopped to produce after 6 days (lag period: II), then achieved their second biogas producing peaks during III period, and gradually reduced after the 14th day (ending period: IV). Biogas summits occurred in No.4 sample in the first 6 days as well, in which biogas was yielded steadily during period of II, then eliminated after the 10th day.

Li considered that microbial community mainly consumed EPS (extracellular polymeric substances) for their own growth at the initial anaerobic digestion period, and then the output of cumulative biogas and daily biogas dropped gradually with the decrease of EPS. In addition, hydrolytic enzyme produced from anaerobic bacterium could dissolve intracellular macromolecules out of microbial cell wall to supply new substrates for methanogens. So thermal hydrolysis method could obviously accelerate this hydrolytic process and raise biogas production finally.

2) Unit biogas Production

After anaerobic biogas production came into stable, unit biogas production and the percentage of methane conversion were shown in Fig.4. Unit biogas production represented the volume of produced methane when per COD of zymotic fluid was degraded after fermentation. Under the circumstances of 35 degree Celsius and 101.3kPa, there would be 395mL pure methane produced when 1gCOD was degraded, so methane conversion rate meant the percentage of the value of COD converted to methane against the total value of COD.

The unit biogas was calculated as follows:

$$G = \frac{G_0 \times 1000}{(C_0 - C_1) \times V_0}$$

G (mL/g)—unit biogas;

G_0 (mL)—cumulative methane production;

C_0 (mg/L)—COD value of SDW before fermentation;

C_1 (mg/L)—COD value of SDW after fermentation;

V_0 (L)—volume of SDW(0.3L).

The results showed that with the increase of zymotic fluid concentration, both unit biogas yield

and methane conversion rate presented first increased and then decreased trend, and the maximum obtained from No.3 sample has occurred (unit biogas yield: 449.8mL/gCOD and methane conversion rate: 95.7%). The order of zymotic fluids according to unit biogas yield was: No.3>No.2>No.4>No.1, which might because the concentration of 450mg/L ammonia nitrogen had been far below the limits of significant inhibition of anaerobic microorganism (1500~3000mg/L). The methanogens with the highest activities could convert the low molecular organic matter (e.g. acetic acid, ethanol) to methane, which had been produced by hydrolytic bacterium. When the concentration of zymotic fluid exceeded No.3 or even No.4, with the increased concentration of ammonia nitrogen, the activities of both acid-forming bacterium and methanogens were inhibited. However, No.4 sample might be its lower concentration, organic matters from zymotic fluid had been consumed by most anaerobic microbes for their growth and metabolism, and the short-chain fatty acids producing methane might be in short supply. Meanwhile, with the rapid increase of concentration of organic matters in zymotic fluid, unit biogas yield appeared plummet trend, which indicated that methanogens' activities had been inhibited obviously by ammonia nitrogen.

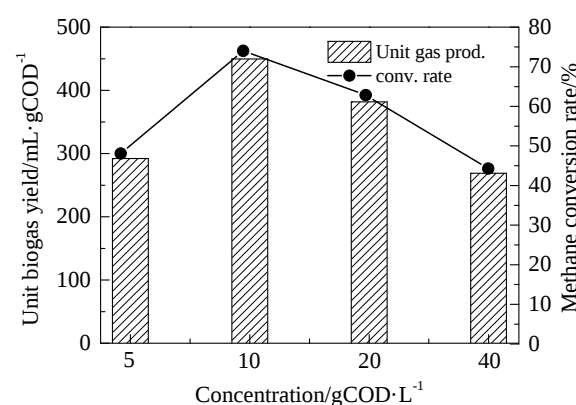


FIG.4 UNIT BIOGAS PRODUCTION AND METHANE CONVERSION OF SLUDGE DEHYDRATED WATER(SDW)

3) Comparative Analysis for Biochemical Methane Potential

Several biogas yield results of anaerobic tests were listed in Table 3 with similar points of anaerobic materials, reaction temperature for methanogens, biogas producing time, and pH range. Because of the different pretreatment methods as well as specific operating conditions during the experiment, it turned out different biogas yield and methane con-

version rate respectively.

Hu stated that methane yield (average methane content 69%) was 50mL/g VS for the mixture of blue algae and anaerobic granular sludge (ratio 6:1). Wang did research on sewage sludge anaerobic digestibility by means of thermal hydrolysis pre-treatment (170°C and 30 minutes) and achieved biogas production rate of 250mL/g COD. Rao adopted three adding rate (5%, 7%, and 10%) in turn during biogas production for 75 days, and achieved the methane yield of 0.12~0.14m³CH₄/kg COD after steady anaerobic operation. Above all, it had an obvious advantage of the sewage sludge for methane production after thermal hydrolysis pre-treatment compared to other means.

TABLE 3 CONTRAST OF BIOCHEMICAL METHANE POTENTIAL WITH SIMILAR ANAEROBIC TESTS

Name	Type	Time /d	Biogas Yield /mL·g ⁻¹ COD	Conv. Rate/%
Hu	batch	—	103.4	20.4
Wang	batch	20	250	44.6
No.3 ¹⁾	batch	20	449.8	74.01
Rao	semi-cont.	75	>260 ²⁾	—

1) No.3: the sample with the concentration of 10COD/L in this paper;
2) Biogas yield was the mean value after steady anaerobic operation.

4) COD and pH of inlet and outlet

The SDW changes of COD and pH before and after fermentation were shown in Table 4. With the increase of zymotic fluids concentration, COD degradation rate reduced gradually, and the pH after fermentation based steadily in weak acid conditions. It might be because too high COD concentration had significantly restrained the acid-forming bacterium

activities, however, the neutral conditions were suitable for methanogens growth. Thus, when syntrophic acetogens converted volatile fatty acids (VFAs, propionic acid, butyric acid, and pentanoic acid) and ethanol to acetic acid, methanogens could convert them to methane. Moreover, due to the pH value after fermentation was higher than its original value, it indicated again the limitation of the SDW fermentation, and more research would be made on how to improve adaptability and activities of acid-forming bacterium for high concentration of COD zymotic fluid.

TABLE 4 CONTRAST OF COD AND pH BEFORE AND AFTER METHANE PRODUCTION

No	COD/g·L ⁻¹		pH	
	Original	Final	Original	Final
1	41.82	25.09	8.82	7.2
2	20.91	4.41	8.87	6.9
3	10.45	1.82	8.86	6.86
4	5.23	0.78	8.9	6.64

In view of unit biogas yield and methane conversion rate, No.3 sample had the optimal results for 449.8mL/gCOD. In consideration of cumulative biogas production and daily biogas production, No.2 sample had the optimal results for 9450mL and the most times of peak values. It would be 1.5 times water consumption additional for the original zymotic fluid diluted to No.3 than that to No.2. However, in view of water consumption, operation costs, and maximal methane production in engineering projects, the organic loading of No.2 sample was optimum value.

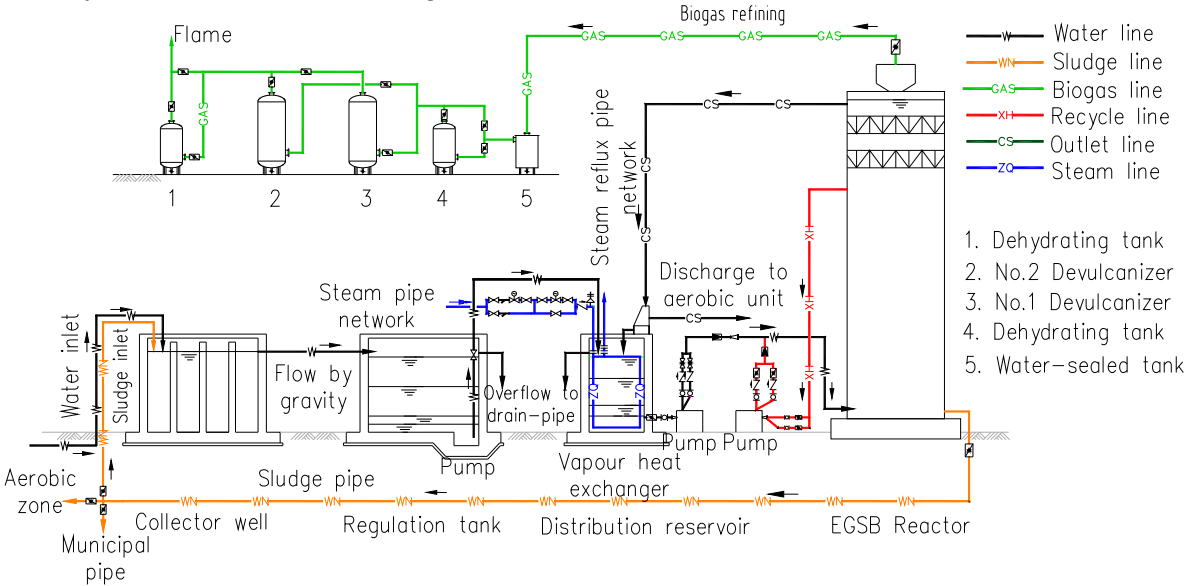


FIG. 5 PROCESS FLOW DIAGRAM OF METHANE PRODUCTION FROM SLUDGE

Engineering of Design and Application

1) Technological Process

By the implementation of the laboratory experiment on methane production potential from sludge hydrothermal drying above, the optimal conditions were determined, and a technical route applied to engineering project was developed. The technological process of methane production from SDW was shown in Fig.5, and aerobic processing unit was connected subsequently to discharge after reaching the standards.

Hydrolytic acidification & EGSB treatment technology were adopted for the anaerobic process of this project. SDW firstly passed through grid drain in order to remove sundries, then entered into collector well. The effluent from collector well as well as partial reflux sewage from aerobic pond flowed into the pre-acidification tank (or regulation tank) to make stable water quality and quantity, where pre-acidification reaction occurred. The outlet flow from regulation tank was pumped into distribution reservoir, and heat was exchanged with hot steam, the temperature of which then could rise to 35 degree Celsius. The effluent from distribution reservoir was pumped into EGSB reactor, where the organic matters of SDW were converted to methane with anaerobic microorganism (e.g. methanogens). Then, the effluent passed through three-phase separator, in which granular sludge was retained in distribution reservoir and mingled with inflow to pass through the EGSB reactor again. After anaerobic digestion, outlet got into the aerobic treatment system subsequently. As well, the methane produced from EGSB reactor could be applied to heat recycling after refining.

The Material and Energy Balance of Sludge Hydrothermal Drying Treatment System

In consideration of the unit of methane production from SDW as the partial of this modification project, it was necessary to investigate the material and energy balance in the whole process, in order to reflect the technical feasibility and advantages of "Hydrothermal Drying & Rotary Kiln Incineration" sludge treatment method. According to the optimal results, the efficiency of 10gCOD/L and 20gCOD/L sample both with 83.42 tons of SDW, if all the loading of COD was degraded, were calculated to produce 210m³ and 342m³ methane, respectively; separately corresponding to the heat from

110kg and 239.5kg standard coal, which could be used for recycling.

Conclusions

With the increase of zymotic fluid concentration, both unit biogas yield and methane conversion rate presented at first increased and then decreased trend, and the maximum obtained from No.3 sample has occurred (unit biogas yield: 449.8mL/gCOD and methane conversion rate: 74.1%). After biogas production, No.3 sample had the maximum of unit biogas yield (449.8mL/gCOD) and methane conversion rate (74.1%), both exceeding to those of No.2 sample (381.8mL/gCOD and 62.84%).

It would be 1.5 times water consumption additional to the original zymotic fluid diluting to No.3 than that to No.2, however, in view of water consumption, operation costs, and maximal methane production in engineering projects, the organic loading of No.2 sample was optimum value.

By carrying out the laboratory experiment on methane production potential from sludge hydrothermal drying, methane production unit from SDW in engineering process was designed. According to the optimal results, the efficiency of 10gCOD/L and 20gCOD/L sample both with 83.42 tons of SDW, if all the loading of COD was degraded, were calculated to produce 210m³ and 342m³ methane, respectively; separately corresponding to the heat from 110kg and 239.5kg standard coal, which could be used for recycling.

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